

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 February 2002 (21.02.2002)

PCT

(10) International Publication Number
WO 02/14240 A1

- (51) International Patent Classification⁷: C07B 63/00, C07C 15/02 // 7/13
- (21) International Application Number: PCT/US01/23528
- (22) International Filing Date: 26 July 2001 (26.07.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/639,555 16 August 2000 (16.08.2000) US
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- (81) Designated States (national): AU, BR, CA, CN, CZ, FI, ID, IN, JP, KR, MX, SG.
- (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).
- Published:
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/14240 A1

(54) Title: REMOVAL OF POLAR CONTAMINANTS FROM AROMATIC FEEDSTOCKS

(57) Abstract: A process for removing polar compounds from an aromatic feedstock containing polar compounds comprising the steps of: (a) contacting the feedstock in an adsorption zone with an adsorbent selective for the adsorption of said polar compounds, said adsorbent comprising a molecular sieve having pores and/or surface cavities with cross-sectional dimensions greater than 5.6 Angstroms and said adsorption zone being at a temperature of less than or equal to 130 °C; and (b) withdrawing from said adsorption zone a treated feedstock which is substantially free of said polar compounds. The resultant treated feedstock is fed to an alkylation zone for contact under liquid phase alkylation conditions with an alkylating agent in the presence of an alkylation catalyst.

REMOVAL OF POLAR CONTAMINANTS
FROM AROMATIC FEEDSTOCKS

Field of the Invention

5 This invention relates to a process for removing polar contaminants from aromatic feedstocks and, in particular, to an aromatic alkylation process employing pretreatment of the aromatic feed to remove nitrogen contaminants.

Background of the Invention

10 In a typical aromatic alkylation process, an aromatic compound is reacted with an alkylating agent, such as an olefin, in the presence of acid catalyst. For example, benzene can be reacted with ethylene or propylene to produce ethylbenzene or cumene, both of which are important intermediates in the chemical industry. In the past, commercial aromatic alkylation processes
15 normally used AlCl_3 or BF_3 as the acid catalyst, but more recently these materials have been replaced by molecular sieve catalysts. Thus, it is known from U.S. Patent No. 4,891,458 to employ a zeolite beta catalyst in the alkylation of aromatic compounds with C_2 to C_4 olefins. In addition, it is known from U.S. Patent No. 4,992,606 to employ MCM-22 in the alkylation of aromatic
20 compounds with short chain (namely having 1-5 carbon atoms) alkylating agents.

 Aromatics alkylation processes employing molecular sieve catalysts can be conducted in either the vapor phase or the liquid phase. However, in view of the improved selectivity and decreased capital and operating costs associated with liquid phase operation, most commercial alkylation processes now operate under
25 at least partial liquid phase conditions. Unfortunately, one disadvantage of operating under liquid phase conditions is that the molecular sieve catalysts tend to be more sensitive to the presence of impurities in the feedstocks, particularly polar compounds such as nitrogen compounds. Such impurities reduce the acid

activity of the catalyst and hence decrease the cycle time between required regenerations of the catalyst.

5 The use of guard beds to remove trace contaminants from hydrocarbon feed streams is well known in the art. This is especially true for petrochemical and specialty chemical operations where product purity is critical. Normally, materials like bentonite clay, kaolin clay or special activated aluminas are used and are placed upstream of a catalyst-containing reaction vessel. The clay or alumina materials trap impurities in the feedstocks so that product purity specifications can be met and poisoning of the catalyst can be reduced. However, 10 known clay and alumina guard beds have limited ability to reduce the basic nitrogen impurities in aromatic feedstreams to the low levels required for use in liquid phase alkylation processes. Moreover, clays are generally not susceptible to regeneration and hence must be discarded when their adsorption capacity is reached.

15 U.S. Patent Nos. 5,744, 686 and 5,942,650 describe processes for the removal of nitrogen compounds from an aromatic hydrocarbon stream by contacting the hydrocarbon stream with a selective adsorbent comprising a non-acidic molecular sieve having a silica to alumina molar ratio in excess of 100 and an average diameter less than 5.5 Angstroms. In both cases the selective 20 adsorbent is a molecular sieve selected from the group consisting of pore-closed zeolite 4A, zeolite 4A, silicalite, F-silicalite, ZSM-5, and mixtures thereof.

PCT Publication No. WO 98/07673 discloses a process for preparing an alkylated benzene or mixture of alkylated benzenes in which the benzene feedstock is initially contacted with a solid acid in a pretreatment zone at a 25 temperature greater than about 130°C and less than about 300°C. The solid acid employed may be an aluminosilicate selected from ZSM-5, ZSM-11, ZSM-35, clinoptilolite, ferrierite, stilbite, EU-1, NU-87, mordenite, zeolite omega, zeolite beta, faujasites, gmelinite, ZSM-12, cancrinite, zeolite L, MCM-22, MCM-41, MCM-49, MCM-56 and MCM-58. The pretreated benzene is then contacted with

an alkylating agent in an alkylation zone or with a transalkylating agent in a transalkylation zone in the presence of an alkylation/transalkylation catalyst which may be selected from mordenite, zeolite beta, ZSM-5, ZSM-12, zeolite Y, zeolite omega, EU-1, NU-87, zeolite L, MCM-22, SSZ-25, MCM-36, MCM-49, MCM-56, MCM-58, and a porous crystalline magnesium silicate.

In accordance with the present invention, it has now been found that molecular sieves having pores and/or surface cavities with a cross-sectional size greater than 5.6 Angstroms are more effective for removing nitrogen contaminants from aromatic feedstocks than the small pore materials described in U.S. Patent Nos. 5,744, 686 and 5,942,650. Moreover, it has been found that the removal can be effected at a temperature less than the 130°C minimum taught in PCT Publication No. WO 98/07673 thereby reducing the formation of by-product hydrocarbon species and hence in potential yield losses, as well as reducing the construction and operating cost of the purification system.

Summary of the Invention

In one aspect, the invention resides in a process for removing polar compounds from an aromatic feedstock containing polar compounds, said process comprising the steps of:

- (a) contacting said feedstock in an adsorption zone with an adsorbent selective for the adsorption of said polar compounds, said adsorbent comprising a molecular sieve having pores and/or surface cavities with cross-sectional dimensions greater than 5.6 Angstroms and said adsorption zone being at a temperature of less than or equal to 130°C; and
- (b) withdrawing from said adsorption zone a treated feedstock which is substantially free of said polar compounds.

The term "substantially free of said polar compounds" is used herein to mean that the treated feedstock contains less than 0.1 ppm, and more preferably less than 0.03 ppm, of said polar compounds.

Preferably, the molecular sieve has pores with cross-sectional dimensions greater than 5.6 Angstroms. More preferably, the molecular sieve is selected from the group consisting of zeolite X, zeolite Y, Ultrastable Y (USY), ZSM-12, mordenite, zeolite beta, zeolite L, and zeolite omega.

5 Alternatively, the molecular sieve has surface cavities with a cross-sectional size greater than 5.6 Angstroms. More preferably, the molecular sieve is selected from the group consisting of MCM-22, MCM-49 and MCM-56.

Preferably, the molecular sieve has a silica to alumina molar ratio less than 100.

10 Preferably, said temperature is 20 to 125°C and most preferably is 25 to 110°C.

In a further aspect, the invention comprises an aromatic alkylation process comprising the steps of:

- 15 (a) contacting an aromatic feedstock containing polar compounds in an adsorption zone with an adsorbent selective for the adsorption of said polar compounds, said adsorbent comprising a molecular sieve having pores and/or surface cavities with a cross-sectional dimensions greater than 5.6 Angstroms and said adsorption zone being at a temperature of less than or equal to 130°C;
- 20 (b) withdrawing from said adsorption zone a treated feedstock which is substantially free of said polar compounds; and
- 25 (c) passing said treated feedstock to an alkylation zone containing an alkylation catalyst comprising a molecular sieve and contacting said treated feedstock with an alkylating agent in said alkylation zone under liquid phase alkylation conditions so as to produce an alkylated aromatic compound.

Preferably, the alkylation catalyst comprises a molecular sieve selected from the group consisting of zeolite beta, MCM-22, MCM-49 and MCM-56.

Detailed Description of the Invention

This invention relates to a process for removing polar contaminants from an aromatic feedstock. More particularly, this invention relates to a liquid phase aromatics alkylation process which includes subjecting the aromatic feedstock to a pretreatment step for the selective removal of polar contaminants that poison aromatic alkylation catalysts. Such contaminants include nitrogen, sulfur, and oxygen containing compounds, particularly those that boil in the same ranges as benzene, toluene or xylenes. Especially problematic are basic nitrogen compounds, such as pyridine, quinoline, N-formyl-morpholine and N-methyl-pyrrolidone, because they neutralize the solid acids that comprise most present day aromatic alkylation catalysts. The process may also be effective for the removal of inorganic cations, particularly salts. For example, depending on the molecular sieve adsorbent employed, the selective sorption process envisioned here may also be able to remove alkali metal cations (Na, K, etc.) and alkaline earth cations (Ca, Mg, etc.) that are problematic in acid catalysis.

The term "aromatic" in reference to the feedstocks which can be treated by the adsorption process of the present invention is used herein in accordance with its art-recognized scope which includes alkyl substituted and unsubstituted mono- and polynuclear compounds.

Substituted aromatic compounds which can be alkylated herein must possess at least one hydrogen atom directly bonded to the aromatic nucleus. The aromatic rings can be substituted with one or more alkyl, aryl, alkaryl, alkoxy, aryloxy, cycloalkyl, halide, and/or other groups which do not interfere with the alkylation reaction.

Suitable unsubstituted aromatic hydrocarbons include benzene, naphthalene, anthracene, naphthacene, perylene, coronene, and phenanthrene, with benzene being preferred.

Generally the alkyl groups which can be present as substituents on the aromatic compound contain from 1 to about 22 carbon atoms and usually from about 1 to 8 carbon atoms, and most usually from about 1 to 4 carbon atoms.

Suitable alkyl substituted aromatic compounds include toluene, xylene, 5 isopropylbenzene, normal propylbenzene, alpha-methylnaphthalene, ethylbenzene, cumene, mesitylene, durene, p-cymene, butylbenzene, pseudocumene, o-diethylbenzene, m-diethylbenzene, p-diethylbenzene, isoamylbenzene, isohexylbenzene, pentaethylbenzene, pentamethylbenzene; 1,2,3,4- tetraethylbenzene; 1,2,3,5-tetramethylbenzene; 1,2,4-triethylbenzene; 10 1,2,3-trimethylbenzene, m-butyltoluene; p-butyltoluene; 3,5-diethyltoluene; o-ethyltoluene; p-ethyltoluene; m-propyltoluene; 4-ethyl-m-xylene; dimethylnaphthalenes; ethylnaphthalene; 2,3-dimethylantracene; 9-ethylanthracene; 2-methylantracene; o-methylantracene; 9,10-dimethylphenanthrene; and 3-methyl-phenanthrene. Higher molecular weight 15 alkylaromatic hydrocarbons can also be used as starting materials and include aromatic hydrocarbons such as are produced by the alkylation of aromatic hydrocarbons with olefin oligomers. Such product are frequently referred to in the art as alkylate and include hexylbenzene, nonylbenzene, dodecylbenzene, pentadecylbenzene, hexyltoluene, nonyltoluene, dodecyltoluene, and 20 pentadecyltoluene. Very often alkylate is obtained as a high boiling fraction in which the alkyl group attached to the aromatic nucleus varies in size from about C₆ to about C₁₂.

Reformate containing substantial quantities of benzene, toluene and/or 25 xylene constitutes a particularly useful feed for the alkylation process of this invention.

Typical feedstocks for use in the process of the invention include benzene, toluene, xylenes and mixtures thereof, with benzene being particularly preferred. As used in commercial alkylation processes, such aromatic feedstocks typically contain from about 0.1 to about 10 ppm, and more typically from about 0.5 to

about 3 ppm of polar impurities. In addition, the feedstocks may contain water up to saturation conditions.

5 The selective sorption process of the invention comprises passing the aromatic feedstock containing polar compounds to an adsorption zone containing an adsorbent selective for the adsorption of said polar compounds, wherein the adsorbent comprises a molecular sieve having pores and/or surface cavities with a cross-sectional dimensions greater than 5.6 Angstroms and the temperature in the adsorption zone is maintained below 130°C, and then withdrawing a treated feedstock which is substantially free of said polar compounds from the adsorption zone.

10 In one embodiment, the molecular sieve used as the adsorbent is a molecular sieve having pores which have average cross-sectional dimensions greater than 5.6 Angstroms. Examples of suitable large pore molecular sieves include zeolite X, zeolite Y, dealuminized zeolite Y, Ultrastable Y (USY), ZSM-12, mordenite, zeolite beta, zeolite L, and zeolite omega. Dealuminized zeolite Y (Deal Y) may be prepared by the method found in U.S. Patent No. 3,442,795. Low sodium Ultrastable Y (USY) is described in U.S. Patent Nos. 3,293,192 and 3,449,070. ZSM-12 is described in U.S. Patent No. 3,832,449. Zeolite beta is described in U.S. Patent No. 3,308,069. A preferred adsorbent is zeolite 13X, which is the sodium form of zeolite X.

20 In an alternative embodiment, the molecular sieve used as the adsorbent is a molecular sieve having surface cavities with a cross-sectional size greater than 5.6 Angstroms. In this case, the pores of the molecular sieve may have cross-sectional dimensions greater, less than or equal to 5.6 Angstroms. Examples of molecular sieves having such surface cavities are MCM-22 (described in U.S. Patent No. 4,954,325), PSH-3 (described in U.S. Patent No. 4,439,409), SSZ-25 (described in U.S. Patent No. 4,826,667), MCM-49 (described in U.S. Patent No. 5,236,575), and MCM-56 (described in U.S. Patent No. 5,362,697).

The molecular sieve used as the adsorbent in the process of the invention

is preferably based on an acidic molecular sieve having a framework silica-to-alumina molar ratio less than 100 and more preferably greater than 10, for example 20 to 50. Higher silica zeolites have been found to be more effective when water is present. However, the higher silica materials also have fewer sites
5 for adsorption and are therefore less effective where the aromatic feedstock is completely free of water.

The molecular sieve used in the adsorption zone of the process of the invention will typically be in the form particles, for example extrudate, spheres or pellets, which contain the molecular sieve together with a binder system to
10 improve physical integrity. The binder system can be any of a number of amorphous metal oxides including alumina, silica, zirconia, and titania, with alumina being preferred.

It is important that the temperature in the adsorption zone is maintained at or below 130°C since operating at higher temperatures is found to increase the
15 formation of by-product hydrocarbon species and hence increase potential yield losses. Moreover, operating the adsorption system at higher temperatures increases the construction and operating cost of the system. Preferably, the temperature in the adsorption zone is 20 to 125 °C and most preferably is 25 to 110°C. Other conditions in the adsorption zone are not critical but generally
20 include a pressure of atmospheric pressure to 1000 psig, and a WHSV of 0.5 to 400 WHSV. The aromatic effluent withdrawn from the adsorption zone is substantially free of polar impurities and typically contains less than 0.1 ppm, and preferably less than 0.03ppm, of polar impurities.

The adsorption zone is normally in the form of a fixed bed in which the
25 aromatic feed stream passes either upflow or downflow through the bed.

In operation, the molecular sieve adsorbent removes polar impurities from the aromatic feedstock until its sorption capacity is reached. At this stage, the adsorbent must be regenerated either by stripping with a desorbent, such as steam or nitrogen, or by heating the adsorbent in air to burn off the sorbed material. In

order to allow continuous treatment of the aromatic feedstock, the adsorption zone may include a plurality of beds of molecular sieve adsorbent so that, as one bed is being regenerated, other bed(s) are available for service.

Where the adsorption step of the present invention is used as a
5 pretreatment for an aromatic feedstock used in an aromatic alkylation process, the adsorption zone is positioned upstream of the aromatic alkylation reactor and effectively protects the alkylation catalyst from polar poisons in the feedstock. The aromatic feedstock is treated in the absence of olefins. Any olefin feed to the alkylation reactor is introduced downstream of the adsorption zone so that no
10 reaction can occur between the aromatic feed stream and any olefins, aside from trace olefins that may be present in the aromatic feed as trace contaminants. In any case, the amount of alkylated aromatics produced by reaction in the adsorption zone is less than 1 wt% of the aromatic feed stream and more typically is less than 0.1 wt% of the aromatic feed stream.

15 After passage through the adsorption zone, the treated aromatic feedstock is fed to an aromatic alkylation reactor containing an aromatic alkylation catalyst where the feedstock is contacted under liquid phase conditions with an alkylating agent.

The alkylating agents useful in the process of this invention generally
20 include any aliphatic or aromatic organic compound having one or more available alkylating aliphatic groups capable of reaction with the aromatic compound, preferably with the alkylating group possessing from 1 to 5 carbon atoms. Examples of suitable alkylating agents are olefins such as ethylene, propylene, the butenes, and the pentenes; alcohols (inclusive of monoalcohols, dialcohols and
25 trialcohols) such as methanol, ethanol, the propanols, the butanols, and the pentanols; aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, and n-valeraldehyde; and alkyl halides such as methyl chloride, ethyl chloride, the propyl chlorides, the butyl chlorides, and the pentyl chlorides.

Mixtures of light olefins are also useful as alkylating agents in the alkylation process of this invention. Accordingly, mixtures of ethylene, propylene, butenes, and/or pentenes which are major constituents of a variety of refinery streams, e.g., fuel gas, gas plant off-gas containing ethylene, propylene, etc., naphtha cracker off-gas containing light olefins, refinery FCC propane/propylene streams, etc., are useful alkylating agents herein. For example, a typical FCC light olefin stream possesses the following composition:

	<u>Wt. %</u>	<u>Mole %</u>
Ethane	3.3	5.1
Ethylene	0.7	1.2
Propane	4.5	15.3
Propylene	42.5	46.8
Isobutane	12.9	10.3
n-Butane	3.3	2.6
Butenes	22.1	18.32
Pentanes	0.7	0.4

The alkylating agents useful in the alkylation process of this invention are preferably olefins having 2 to 5 carbon atoms and most preferably ethylene or propylene. Reaction products which may be obtained from the process of the invention include ethylbenzene from the reaction of benzene with ethylene, cumene from the reaction of benzene with propylene, ethyltoluene from the reaction of toluene with ethylene, cymenes from the reaction of toluene with propylene, and sec-butylbenzene from the reaction of benzene and n-butenes. The preferred reaction products are ethylbenzene and cumene.

The aromatic alkylation catalyst is a molecular sieve and preferably is a molecular sieve selected from zeolite beta, MCM-22, MCM-49 and MCM-56. The same molecular sieve can be used in the alkylation reactor as that used for the adsorption zone.

The alkylation step of this invention is conveniently conducted under conditions including a temperature of 0° to 500°C, and preferably 50° to 250°C, a pressure of 0.2 to 250 atmospheres, and preferably 5 to 100 atmospheres, a molar

ratio of alkylatable aromatic compound to alkylating agent of 0.1:1 to 50:1, and preferably 0.5:1 to 10:1, and a feed weight hourly space velocity (WHSV) of 0.1 to 500 hr⁻¹, preferably 0.5 to 100 hr⁻¹.

5 When benzene is alkylated with ethylene to produce ethylbenzene, the alkylation reaction is preferably carried out under conditions including a temperature between 300° and 600°F (150° and 316°C), preferably between 400° and 500°F (205° and 260°C), a pressure up to 3000 psig (20875 kPa), preferably between 400 and 800 psig (2860 and 5600 kPa), a space velocity between 0.1 and 20 WHSV, preferably between 1 and 6 WHSV, based on the ethylene feed, and a
10 ratio of the benzene to the ethylene in the alkylation reactor from 1:1 to 30:1 molar, preferably from 1:1 to 10:1 molar.

When benzene is alkylated with propylene to produce cumene, the reaction is preferably carried out under conditions including a temperature of up to 250°C, e.g., up to 150°C, e.g., from 10° to 125°C; a pressure of 250 atmospheres or less,
15 e.g., from 1 to 30 atmospheres; and an aromatic hydrocarbon weight hourly space velocity (WHSV) of from 5 hr⁻¹ to 250 hr⁻¹, preferably from 5 hr⁻¹ to 50 hr⁻¹.

The aromatic compound reacts with the alkylating agent in the alkylation reactor to produce the desired monoalkylated aromatic product, for example ethylbenzene or cumene. However, the alkylation product stream will inevitably
20 contain polyalkylated species which are preferably separated and fed to a transalkylation zone for reaction with additional alkylatable aromatic compound, such as benzene, in the presence of a transalkylation catalyst. The transalkylation catalyst is preferably selected from zeolite beta, TEA-mordenite, MCM-22, MCM-49 and MCM-56. The transalkylation reaction is also preferably conducted
25 under liquid phase conditions.

The invention will now be more particularly described with reference to the following examples.

Example 1 (Comparative)

A mixture of 1 part by weight acetonitrile in 99 parts by weight toluene was prepared using reagent grade toluene and acetonitrile. A series of batch runs was carried out with ZSM-5 zeolite having a silica-to-alumina molar ratio of 26 as the adsorbent. Prior to contact with the acetonitrile:toluene mixture, the ZSM-5 was activated by calcination at 500°C. In each run, a fixed volume of the toluene:acetonitrile solution was contacted with varying amounts of dry adsorbent in a glass container at 25°C and atmospheric pressure. After 12 hours gas chromatographic analysis of the solution was carried out, with 2 wt% 2,3 dimethylbutane being added to the solution as an internal reference. The results of the experiments are given in Table 1 below:

Table 1Adsorption of Acetonitrile by ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 26:1$)

Solution Charge, ml	Adsorbent Charge, g	Equilibrium Acetonitrile Concentration, wt%	Acetonitrile Adsorbed, mg/gram of adsorbent
10	3.6	0.029	22.7
10	3.15	0.033	25.8
10	1.84	0.146	39.0
10	1.60	0.201	41.9
10	1.20	0.336	46.2
10	0.54	0.645	54.4

At equilibrium, the uptake of acetonitrile by the ZSM-5 adsorbent was approximately 55 mg/g of adsorbent.

Example 2 (Comparative)

A mixture of 1 part by weight acetonitrile in 99 parts by weight toluene was prepared using reagent grade toluene and acetonitrile. A series of batch runs was carried out with another sample of ZSM-5 zeolite that had a silica-to-alumina molar ratio of 700. Prior to contact with the acetonitrile:toluene mixture, the ZSM-5 was activated by calcination at 500°C. In the same manner as in Example 1, a fixed volume of the toluene:acetonitrile solution was contacted with varying

amounts of dry adsorbent in a glass container at 25°C and atmospheric pressure. After 12 hours gas chromatographic analysis of the solution was carried out, with 2 wt% 2,3 dimethylbutane being added to the solution as an internal reference. The results of the experiments are given in Table 2 below:

5

Table 2
Adsorption of Acetonitrile by ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 700:1$)

Solution Charge, ml	Adsorbent Charge, g	Equilibrium Acetonitrile Concentration, wt%	Acetonitrile Adsorbed, Mg/gram of adsorbent
10	4.20	0.092	18.2
10	3.88	0.072	20.1
10	2.05	0.235	31.1
10	1.65	0.271	36.8
10	1.43	0.325	39.3
10	0.71	0.577	48.9

10

At equilibrium, the uptake of acetonitrile by the ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 700:1$) adsorbent was approximately 49 mg/g of adsorbent, which is slightly lower than the value obtained in Example 1.

15

Example 3

20

A mixture of 1 part by weight acetonitrile in 99 parts by weight toluene was prepared using reagent grade toluene and acetonitrile. A series of batch runs was carried out with a sample of MCM-22 zeolite that had a silica-to-alumina ratio of 26:1. Prior to contact with the acetonitrile:toluene mixture, the MCM-22 was activated by calcination at 500°C. In the same manner as in Example 1, a fixed volume of the toluene:acetonitrile solution was contacted with varying amounts of dry adsorbent in a glass container at 25°C and atmospheric pressure. After 12 hours gas chromatographic analysis of the solution was carried out, with 2 wt% 2,3 dimethylbutane being added to the solution as an internal reference. The results of the experiments are given in Table 3 below:

25

Table 3Adsorption of Acetonitrile by MCM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 26:1$)

Solution Charge, ml	Adsorbent Charge, g	Equilibrium Acetonitrile Concentration, wt%	Acetonitrile Adsorbed, mg/gram of adsorbent
10	4.48	0.000	18.7
10	3.90	0.000	21.6
10	2.80	0.012	29.6
10	2.14	0.048	37.6
10	1.32	0.203	50.6
10	0.76	0.454	59.4
10	0.71	0.484	60.0

5 At equilibrium, the uptake of acetonitrile by the MCM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 26:1$) adsorbent was approximately 60 mg/g of adsorbent, which is higher than that obtained in either Example 1 or 2. In addition, the MCM-22 adsorbent was more effective in removing acetonitrile from solutions at the higher loadings of acetonitrile. Complete removal of acetonitrile was achieved.

10

Example 4

A mixture of 1 part by weight acetonitrile in 99 parts by weight toluene was prepared using reagent grade toluene and acetonitrile. A series of batch runs was carried out with a sample of 13X zeolite that had a silica-to-alumina ratio of 2.5:1 and which had been activated by calcination at 500°C. In the same manner as in Example 1, a fixed volume of the toluene:acetonitrile solution was contacted with varying amounts of dry adsorbent in a glass container at 25°C and atmospheric pressure. After 12 hours gas chromatographic analysis of the solution was carried out, with 2 wt% 2,3 dimethylbutane being added to the solution as an internal reference. The results of the experiments are given in Table 4, below:

20

Table 4Adsorption of Acetonitrile by 13X ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.5:1$)

Solution Charge, ml	Adsorbent Charge, g	Equilibrium Acetonitrile Concentration, wt%	Acetonitrile Adsorbed, mg/gram of adsorbent
10	5.83	0.004	14.4
10	3.72	0.007	22.5
10	2.23	0.014	37.2
10	1.68	0.030	48.5
10	0.74	0.085	103.7

At equilibrium, the uptake of acetonitrile by the 13X adsorbent was at least 103 mg/g of adsorbent, which is higher than that obtained in either Example 1, 2, or 3.

Example 5

A solution was prepared containing 25 ppm of N-formyl-morpholine and 200 ppm water and was contacted with various molecular sieve adsorbents under a nitrogen atmosphere and at reflux conditions of about 110°C. After 24 hours the amount of nitrogen remaining in the solution and the amount of nitrogen adsorbed by the adsorbent, were measured by chemiluminescence. The results are shown in Table 5.

Table 5

Adsorbent	Mass of Adsorbent	"N" in Solution	"N" in Adsorbent
USY			
250mL solution	0.02	24	9750
50mL solution	0.1	1.3	5500
50mL solution	1	1	859
50mL solution	5	1	331
13X			
250mL solution	0.02	24	9500
50mL solution	0.1	7.6	6200
50mL solution	1	1	215
50mL solution	5	1	180
Spent MCM-22			
250mL solution	0.02	28	3500
50mL solution	0.1	20	1800
50mL solution	1	1	1200
50mL solution	5	1	148

5 The spent MCM-22 was a catalyst which had been used in a commercial cumene plant and which had been regenerated after removal from the plant at the end of its useful life.

Whereas each sieve tested showed activity for the removal of the N-formyl-morpholine, the USY and 13X exhibited higher sorption capacity than spent MCM-22.

CLAIMS:

1. A process for removing polar compounds from an aromatic feedstock containing polar compounds, said process comprising the steps of:
 - 5 (a) contacting said feedstock in an adsorption zone with an adsorbent selective for the adsorption of said polar compounds, said adsorbent comprising a molecular sieve having pores and/or surface cavities with cross-sectional dimensions greater than 5.6 Angstroms and said adsorption zone being at a temperature of less
10 than or equal to 130°C; and
 - (b) withdrawing from said adsorption zone a treated feedstock which is substantially free of said polar compounds.
2. The process of claim 1, wherein the molecular sieve has pores with
15 cross-sectional dimensions greater than 5.6 Angstroms.
3. The process of claim 2, wherein the molecular sieve is selected from the group consisting of zeolite X, zeolite Y, Ultrastable Y (USY), ZSM-12, mordenite, zeolite beta, zeolite L, and zeolite omega.
20
4. The process of claim 1, wherein the molecular sieve has surface cavities with a cross-sectional size greater than 5.6 Angstroms.
5. The process of claim 4, wherein the molecular sieve is selected
25 from the group consisting of MCM-22, MCM-49 and MCM-56.
6. The process of claim 1, wherein the molecular sieve has a silica to alumina molar ratio less than 100.
- 30 7. The process of claim 1, wherein said temperature is 20 to 125°C.

8. The process of claim 1, wherein said temperature is 25 to 110°C.
9. The process of claim 1, wherein the treated feedstock contains less
5 than 0.1 ppm of said polar compounds.
10. An aromatic alkylation process comprising the steps of:
- (a) contacting an aromatic feedstock containing polar
10 compounds in an adsorption zone with an adsorbent
selective for the adsorption of said polar compounds, said
adsorbent comprising a molecular sieve having pores and/or
surface cavities with a cross-sectional dimensions greater
than 5.6 Angstroms and said adsorption zone being at a
temperature of less than or equal to 130°C;
- 15 (b) withdrawing from said adsorption zone a treated feedstock
which is substantially free of said polar compounds; and
- (c) passing said treated feedstock to an alkylation zone
20 containing an alkylation catalyst comprising a molecular
sieve and contacting said treated feedstock with an
alkylating agent in said alkylation zone under liquid phase
alkylation conditions so as to produce an alkylated aromatic
compound.
11. The process of claim 10, wherein the alkylation catalyst comprises
25 a molecular sieve selected from the group consisting of zeolite beta, MCM-22,
MCM-49 and MCM-56.
12. The process of claim 10, wherein the aromatic feedstock is benzene
and alkylating agent is ethylene or propylene

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/23528

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07B63/00 C07C15/02 //C07C7/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C07B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 07673 A (THE DOW CHEMICAL COMPANY) 26 February 1998 (1998-02-26) cited in the application page 3 -page 4 page 6 -page 9 claims	1-6,9-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

6 December 2001

Date of mailing of the international search report

18/12/2001

Name and mailing address of the ISA

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-11 (in part)

Present claims 1 and 10 relate to an extremely large number of possible compounds used as feedstock and/or alkylating agent. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds of which the use as feedstock or alkylating agent is claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds used as feedstock listed from line 25 of page 5, to line 22 of page 6 and the alkylating agents listed from line 23 of page 9, to line line 6 of page 10.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No
PCT/US 01/23528

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9807673	A	26-02-1998	
		AU 4077797 A	06-03-1998
		CN 1228073 A	08-09-1999
		EP 0922020 A1	16-06-1999
		JP 2000516248 T	05-12-2000
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